

THE EFFECT OF FILLER LOADING ON THE TENSILE STRENGTH OF
NATURAL RUBBER COMPOUND

JUAN ANAK TUGAU

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Faculty of Chemical Engineering and Natural Resource
Universiti Malaysia Pahang

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ABSTRACT

The effects of Carbon Black fillers loading on the Tensile Strength of Natural rubber (SMR) compound were investigated in this study. In this study, 5 KN forces were used to determine Tensile Strength for each ingredient of Rubber compounds are reinforced with filler such carbon black. In general, Natural Rubber (SMR) prepare in range 10 phr, 30 phr and 50 phr of Carbon Black N220 filler loading. The Natural Rubber (SMR) composition also filled with additives such as stearic acid, CBS, zinc white and antioxidant like Aromatic oil meanwhile vulcanization accelerator, and vulcanizing agent like sulphur after 3 hour cool down under room temperature. After 24 hour cooled under room temperature, molding process should be run. After molding, the sample should be cooled under room temperature around 2 days before tensile process. In generally, the amount of the filler added is around 50 parts by weight per 100 parts by weight of the rubber component based on standard ingredient. When the amount of the filler is less by weight, the reinforcing property is insufficient and the wear resistance is poor, while when it exceeds 200 parts by weight, the tensile Strength really strong and the sample become waste because too hard for processing..

ABSTRAK

Mengkaji kesan campuran Karbon Hitam N220 (CB) ke atas Kekuatan Tegangan Getah semula jadi (SMR) telah dikaji dalam kajian ini. Dalam kajian ini, daya sebanyak 5 KN digunakan untuk menentukan Kekuatan Tegangan setiap resipi campuran getah SMR. Dalam kajian ini juga, SMR disediakan dengan berlainan kuantiti CB N220 yang digunakan, diantara nya ialah, untuk eksperimen 1, 10 Phr CB N220 digunakan diikuti 30 phr CB N220 dan 50 phr CB N220. Selain itu, terdapat juga bahan kimia lain ditambah satu per satu seperti zink oksida, asid stearik, CBS dan anti- oksida seperti minyak aromatik. Sementara Pencepat Vulkanizasion dan agen Vulkanizasion seperti sulfur ditambah selepas campuran awal tersebut dibiarkan selama 3 jam setelah dibiarkan dibawah suhu bilik. Setelah proses itu selesai, campuran tersebut dibiarkan selama 24 jam dibawah suhu bilik sebelum proses seterusnya iaitu ‘molding’ yang dibentuk mengikut piawai yang telah sedia ada. Selepas sahaja proses ‘molding’ selesai, ujian kekuatan Tegangan dijalankan. Pada umumnya, kuantiti Karbon Hitam digunakan ialah 50 Phr untuk maksimum daripada 165 jumlah berat resipi piawai campuran getah. Jika kuantiti Karbon Hitam kurang, sifat-sifat campuran getah tersebut menjadi sangat lemah dan tidak ada kekuatan tegangan yang dkehendaki. Manakala, jika kuantiti berlebihan juga, campuran getah tersebut sangat-sangat kuat sehingga susah hendak diproses.

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LIST OF ABBREVIATION

ABBREVIATION	FULL NAME
CB	Carbon Black
CBS	n-(1,3-dimethylbutyl)-n-phenylenediamine
IPPD	Isopropylene-n-phenyl-p-phenylenediamine
PHR	Part Hundred of Rubber
SMR	Standard Malaysia of Rubber (Natural Rubber)

CHAPTER 1

INTRODUCTION

1.0 Background Study

History of Natural Rubber (NR) was started around 500 year ago. Christopher Columbus who was started the history of natural rubber when he returned from his second voyage, bringing back the first rubber ball from West Indies. Then, Spanish starting the revolution of rubber when them already discovered of the used of latex for the water proofing of leather and fabric in 1615. In 1818, the rubber industry in Europe started by Charles Mancintosh. After 2 year, Thomas Hancock discovered mastication. Year after year the revolutions was expansion around the west, it also came to Malaysia in late 1890's until today. It begins in peninsular Malaysia and Asian.

The term 'rubber' originally meant material obtained from the rubber tree *heavea brasiliensis*. Today, a distinction is made between crude rubber and vulcanized rubber, or elastomer. For over a century, all rubber goods were manufactured from natural rubber, which is generated in the rubber tree as a milky liquid (emulsion) known as natural latex (A. Ciesielski, 1988). The latter is coagulated and the solid material separated, washed and dried to obtain a solid natural crude rubber. Later, man-made synthetic crude rubbers were developed and became available in commercial quantities.

Although natural rubber is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvements in processing.(Peter A. Ciullo,1999) Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus. In most applications, carbon black (CB) and silica have been used as the main reinforcing fillers that increase the usefulness of rubbers. When CB is compounded with rubbers, tensile strength, tear strength, modulus and abrasion resistance are increased. For this reason, CB has been extensively exploited in numerous rubber engineering products. In general, a CB-reinforced rubber has a higher modulus than a silica-reinforced one.(Z. H. Li, J. Zhang, 1998)

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in structural applications. The force per unit area (MPa or psi) required to break a material in such a manner is the ultimate tensile strength or tensile strength at break. (Jareerat Ruamcharoen , 2001)The rate at which a sample is pulled apart in the test can range from 0.2 to 20 inches per minute and will influence the results. The analogous test to measure tensile properties in the ISO system is ISO 527. The values reported in the ASTM D638 and ISO 527 tests in general do not vary significantly and either test will provide good results early in the material selection process. Separate tensile test methods are commonly applied to polymer films (ASTM D882) and elastomers (ASTM D412).(J. S. Dick, 2001).

The ultimate elongation of an engineering material is the percentage increase in length that occurs before it breaks under tension. Ultimate elongation values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid rubber, especially fiber reinforced ones, often exhibit values under 5%. The combination of high ultimate tensile strength and high elongation leads to materials of high toughness.

The tensile modulus is the ratio of stress to elastic strain in tension. A high tensile modulus means that the material is rigid - more stress is required to produce a given amount of strain. In polymers, the tensile modulus and compressive modulus can be close or may vary widely. This variation may be 50% or more, depending on resin type, reinforcing agents, and processing methods. The tensile and compressive moduli are often very close for metals. (Jareerat Ruamcharoen, 2001)

1.2 Problem Statement

There are several problem can occur that can influent the tensile properties of rubber compound. Temperature was one of a major factor that cans influent physical properties of rubber compound. Basically temperatures were used for molding process at 150 °C until 180°C. Different temperature has different tensile strength. Besides, the heating period in molding process can influent of tensile strength of rubber compound.

Processing errors committed during the manufacture can seriously affect the properties of the final product. For example, too much milling of the rubber in the mixing mill or in the internal mixer can give a product of low strength.

Besides that, quantity of filler either carbon black and non carbon black as a major factor to influent the tensile properties of rubber compound. Generally, filler loading at 50 Phr in ingredient of rubber compound based on standard. But, problem will occur when content filler was too low and excess that 50 phr. That product will become useless and hard to process for produced a good product. Finally, it becomes waste to environment.

1.3. Objective of the Study

The main objective for this research is to study the effect of Carbon Black filler loading on the Tensile strength of Natural rubber compound

2.4. Scope of Research Work

In order to achieve the objective, there are several scope was have been identified

1. To study effect of carbon black N220 filler loading on the Tensile Strength of Natural rubber (SMR) compound formulation by using Force, 5 KN load
2. To study Tensile Strength of 10 phr,30 phr,50 phr of carbon black N220 filler loading to SMR compound.
3. To study Tensile Strength of 10 phr,30 phr,50 phr of carbon black N220 filler loading to SMR compound through molding and compress process in 10 minutes

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A rubber compound contains, on average, less than 5 lbs. of chemical additives per 100 lbs. of elastomeric, while filler loading is typically 10-15 times higher. Of the ingredients used to modify the properties of rubber products, the filler often plays a significant role. Most of the rubber fillers used today offers some functional benefit that contributes to the process ability or utility of the rubber product. Styrene-butadiene rubber, for example, has virtually no commercial use as an unfilled compound.(Brendan Rodger, 2001)

Some confusion may arise because term such rubber compound and compounding are used where strictly the terms rubber mixture and mixing, respectively, should be used. By rubber compounding is meant the way of making useful products from crude rubber.

The first step of rubber compounding is usually to soften the crude rubber by mechanical working. This can be done on two-roll mills or in internal mixer. In this soft condition the rubber is easily blended with a variety of compounding ingredients that are normally given in parts per weight, based on 100 parts of crude rubber (phr). A generalized rubber formula is given in table 2.1. Rubber formulas are almost never publicized by manufacturers.(Peter A. Ciullo and Norman Hewit,1999)

Material	Part per Weight	Function
Raw rubber	100	The main component in rubber compounding
Filler	50	To modified the mechanical properties and reduced cost
Softener	5	To ease the processing, to modify the specific properties.
Anti oxidant	1	To protect the rubber from aging(an irreversible change in material properties after expose to environment
Accelerator	1	To increase vulcanization process and reduce the time of vulcanization
Zinc oxide	5	As activator to increase the accelerator efficiency
Stearic acid	1	As activator to increase the accelerator efficiency
Sulphur	2	To produced a cross linking

Table 2.1 Generalized rubber formula

Each ingredient has a specific function, either in processing, vulcanization or end use of the product. The various ingredients may be classified according to their specifics function in the following groups:

1. Filler (carbon black, whiting and china clay filler)
2. Plasticizer or softeners(extenders, processing aid, special plasticizer)
3. Age resistors or anti-degradants(antioxidants, antiozonants, special age resistors, protective waxes)
4. Vulcanizing or curing ingredients(vulcanizing agents, accelerator, activators)

5. Special-purpose ingredients(coloring pigments, blowing agents, flame retardants, odorants, antistatic agent, retarders, peptizes)

2.2 Fillers

Filler are compounding ingredients, usually in powder form, added to crude rubber in relatively large proportions (typically 50 phr). They include two major groups, carbon blacks and non-carbon black filler. Carbon black consists mainly of finely divided carbon manufactured by incomplete combustion of natural gas or petroleum using different process. The non-black filler include whiting and china clay.

Clay is also used as a semi-reinforcing agent for rubber, and about 900 million pounds is used per year in the U.S. Most is hard clay mined in Georgia and South Carolina. It is used in tire carcasses, sidewalls, and bead insulation. Clay offers some reinforcement to the rubber compound but less than reinforcing grades of carbon black.

Ground and precipitated calcium carbonate is used in rubber compounds. The ground products are added as extender fillers, while the precipitated types offer some reinforcement due to their small particle size. It is reported that over one billion pounds of calcium carbonate is used in rubber compounds in the U.S. per year

Filler are added for economic or technical purpose. Some are incorporated primarily to extend and therefore make the final product less expensive and others mainly to reinforce it. By reinforcement is meant enhancement of properties such as tensile strength, tear, and abrasion resistance (D. T. Norman, 1978). Consequently, filler may be classified into two broad groups: reinforcing and non-reinforcing, or active and

inactive. However, the distinction between the two groups is not clear-cut because many fillers exhibit intermediate properties.

A rubber compound contains, on average, less than 5 lbs of chemical additives per 100 lbs of elastomer. Filler loading is typically 10 to 15 times higher. Of the ingredients used to modify the properties of rubber products, the filler plays a dominant role. The term ‘filler’ is misleading, implying, as it does, a material intended primarily to occupy space and act as a cheap diluents of more costly elastomer. Most of the rubber filler used today offer some functional benefit that contributes to the process ability or utility of rubber product. Styrene-butadiene rubber, for example, currently the highest volume elastomer, has virtually no commercial use as an unfilled compound.

2.2.1 Filler Properties

The characteristics which determine the properties filler will impact to a rubber compound are particle size, surface, structure, and surface activity. (D. T. Norman, 1978).

2.2.1.1 Particle Size

If the size of filler particles greatly exceeds the polymer inter-chain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Filler with particles size greater than 10,000 nm are therefore generally avoided because they can reduce performance rather than reinforce or extend. Fillers with particles size between 1,000 and 10,000 nm are used primarily as diluents and usually have no significant affect, positive or negative, on rubber properties. Semi-

reinforcing filler, which range from 100 to 1,000 nm, improve strength and modulus properties, the truly reinforcing fillers, which range 10 to 100nm significantly, improve rubber properties

Of the approximately 2.1 million tons of filler used in rubber each year, 70% is carbon black, 15% is kaolin clay or china clay, 8% is calcium carbonate or whiting, 4% is the precipitated silica and silicates and the balance is variety of miscellaneous minerals.(D. T. Norman,1978). Figure 2.2.1.1 classifies the various filler by particles size and consequent reinforcement potential

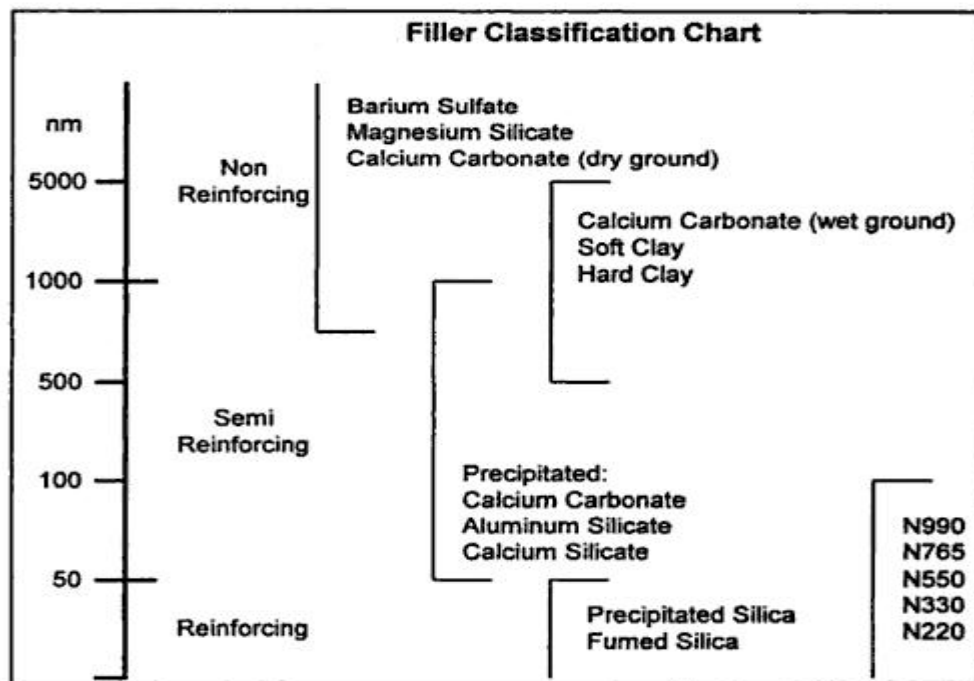


Figure 2.2.1.1 Filler Classification Chart

Most talcs and dry –ground calcium carbonates are degrading filler because of their large particles size; although the planar shape of the talc particles contributes some improvement in reinforcement potential. The soft clays would fall into a class of diluents fillers that do not contribute reinforcement, yet are not large that they degrade properties.(D. T. Norman,1978).

The hard clays contribute some reinforcement to rubber compounds, primarily because of their smaller particle size and are normally classified as the semi-reinforcing class. The carbon black is available in various particles sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.(Z. H. Li, J. Zhang, S. J. Chen, 1998)

2.2.1.2 Surface Area

Particle size is generally the inverse surface area. Filler must make intimate contact with elastomer chains if it is going to contribute to reinforcement. Filler that have high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surfaces available for contacting the rubber than spherical particles with an equivalent average particle diameter. Clays have planar-shaped particles that align with the rubber chains during mixing and processing, and thus contribute more reinforcement than a spherical-shape calcium carbonate particle of similar average particle size.(Z. H. Li, J. Zhang, S. J. Chen, 1998).Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerable smaller than the particles of clay. They thus have more surfaces per

unit weight available to make contact with the polymer. Rubber grade carbon black varies from 6 to 259 m²/g.

2.2.1.3 Structure

The shape of an individual particle of reinforcing filler like carbon black is of less importance than the filler's effective shape once dispersed in elastomer. The black used for reinforcement have generally round primary particles but function as anisometric acicular aggregates. These aggregate properties-shapes, density, size-define their structure. High structure filler has aggregates favoring high particle count, with those particles joined in chain like cluster from which random branching of additional particle may occur. In simplest term, the more an aggregate deviates from solid spherical shape and the larger its size, the higher is its structure. The higher its structure, in turn, the greater it's reinforcing potential. (Chayanoot Sangwichien.,2008; Z. H. Li, J. Zhang, S. J. Chen, 1998)

For reinforcing, fillers which exist as aggregates rather than discrete particles, carbon black in particular, a certain amount of structure that existed at manufacture is lost after compounding. The shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. (Chayanoot Sangwichien,2008). The structure that exist in the rubber compound, the persistent structure, is what affects process ability and properties

2.2.1.4 Surface Activity

A filler can offer high surface area and high structure but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to non-polar elastomer; polar filler work best in polar elastomers. Beyond this general chemical compatibility is potential for reaction between the elastomer and active sites on the filler surfaces. Carbon black particles, for example, have carboxyl, lactone quinone, and other organic functional groups which promote a high affinity of rubber to filler. This together with the high surface area of the black means that there will be intimate elastomer-black contact. The black also has a limited number of chemically active sites (less than 5% of total surface) which arise from broken carbon-carbon bonds as a consequence of the methods used to manufacture the black. (Z.H.Li, J. Zhang, S. J. Chen, 1998). The close contact of elastomer and carbon black will allow these active sites to chemically react with elastomer chains. The carbon black particle effectively becomes a crosslink. The non-black filler generally offer less affinity and less surface activity toward the common elastomers. (Chayanoot Sangwichien, 2008)

2.2.2 Filler Effects

The principal characteristics of rubber fillers-particle size, surface area, structure, and surface activity-are interdependent in improving rubber properties. In considering fillers of adequately small particles size reinforcement potential can be qualitatively small particles size, reinforcement potential can be qualitatively considered as the product of surface area, surface activity, and persistent structure or anisometry (planar or acicular nature).(P. Threepopnatkul,2003)

The general influence of each of these three filler characteristics above on rubber properties can be summarized as follows:

1. Increasing surface area or decreasing particle size gives lower resilience and higher Mooney Viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis.
2. Increasing surface activity including surface treatment gives higher abrasion resistance, chemical adsorption or reaction, modulus (at elongation>300%), and hysteresis.
3. Increasing persistent structure/anisometry gives higher Mooney Viscosity, modulus (at elongation<300%), and hysteresis, lower extrusion shrinkage, tear resistance, and resilience, and longer incorporation time

2.2.2.1 Modulus

Modulus is a measure of the force required to stretch a defined specimen of rubber to a given percent elongation. A filler with low surface activity will increase resistance to elongation by the viscous drag it surface provides to the polymer trying to stretch and slide around it. Higher surface area, greater anisomery or structure, and higher loading will all increase the modulus. (P. Threepopnatkul, 2003; Chayanoot Sangwichien, 2008; Z. H. Li, J. Zhang, S. J. Chen, 1998)

It is helpful to visualize the filler particles acting as giant cross-links. Figure 2.2.2.1 is a schematic representation of such a system with the filler particles simplified to spheres of convenience. Before stretching (step 1), the polymer chains are in random configuration. Chains A, B and C have multiple points of attachment to the filler particles, corresponding to the latter's active sites. On elongation, resistance is supplied as the energy required detaching that chain segments these active sites (step 2 and 3). The amount energy required to attain maximum elongation, and then required to overcome the stress distribution implied in step 3 to cleave chain-chain and chain-filler attachments, like wise explains the higher tensile strength of a system of this type.

After the elongating force has been removed, the elastomer chains return to their preferred random orientation(step 4), except that now they have the minimum number of points of attachment to the filler as a consequence of having been extended, as in step 3. Less force would now be required to return these chains to ultimate extension, because the intermediate points of attachment that existed in step 1 and step 2 have been eliminated. This accounts for the phenomenon known to rubber technologists as stress softening. With repeated stress-relaxation cycling, a decrease in modulus form the initial maximum is obtained. Stress softening is a temporary effect. After a period without

strain, the rubber will recover to near its original modulus, as the active filler sites again attach to polymer segments. (P. Threepopnatkul, 2003). A percentage of original modulus is permanently lost, however, due to irrecoverable chain and bond cleavage.

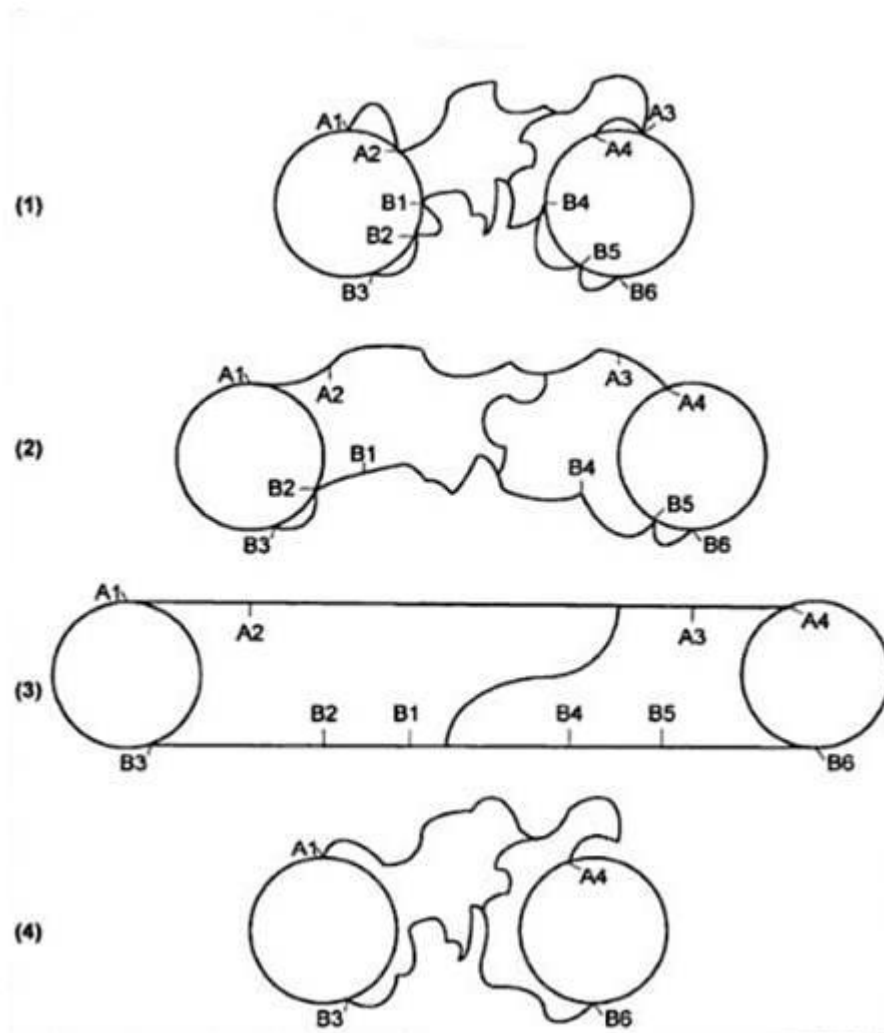


Figure 2.2.2.1 Filler cross-linking